(19) (CA) **CANADIAN PATENT** (12)

(54) CATALYSIS

(72) Knight, Stephen J.,
U.K.

(73) Granted to Johnson, Matthey & Co., Limited
U.K.

ABSTRACT OF DISCLOSURE

This invention relates to catalytic processes for the purification of air and other gaseous media, for example, exhaust gases from industrial plant and automobiles. In particular, the invention is concerned with contacting the gas at an elevated temperature with a catalyst comprising one or more of the metals platinum, rhodium, iridium, osmium, palladium, ruthenium, gold and silver supported on or associated with a refractory oxide support made from silica, alumina or mixtures or compositions containing silica and/or alumina.

This invention relates to a catalytic process for use in the purification of air and other gaseous media. More particularly, it relates to the catalytic removal of one or more oxides of nitrogen, especially in the presence of excess oxygen, and also to the catalytic removal of carbon monoxide and organic compounds such as the lower hydrocarbons.

The exhaust gases from an internal combustion engine include oxygen, carbon monoxide, unburnt hydrocarbons and nitrogen oxides. If the engine is fuelled by petrol, the oxygen is generally present in a stoichiometrically lean concentration, that is, the atmosphere is a "net reducing atmosphere". Under such conditions, the nitrogen oxides may be catalytically reduced in one catalyst bed and the carbon monoxide and hydrocarbons may be mixed with additional oxygen and catalytically oxidised in a second catalyst bed. If, on the other hand, the engine is fuelled by diesel, there is a stoichiometric excess of oxygen in the exhaust gases and the nitrogen oxides may only be catalytically reduced after adding an excess of a reducing fuel. The exhaust of a petrol-fuelled internal combustion engine will also be oxygen-rich under certain operating conditions.

In the manufacture of nitric acid, tail gases contain appreciable quantities of NO and other oxides of nitrogen which it is desirable to remove before venting

to atmosphere.

According to one feature of the invention, a process for the catalytic removal of oxides of nitrogen present in a gas comprises contacting the gas at elevated temperature with a catalyst comprising one or more metals from the platinum group, gold and silver, supported on or associated with a refractory oxide.

By "the platinum group" we mean platinum, rhodium, iridium, osmium, palladium and ruthenium, and of these we particularly prefer to use platinum, rhodium or iridium. The metals may be alloyed together, or may be present as a mixture or alloy with one or more base metals or one or more precious metals, other than those of the platinum group.

The refractory oxide may be an oxide or a mixture of oxides of elements of Groups IIA, IIB or IVB of the Periodic Table, or of the transition metals. Such elements are, for example, beryllium, magnesium, calcium, scandium, yttrium, titanium, zirconium, aluminium, silicon or germanium. Additionally, such compounds as the aluminosilicates may be used. We prefer to use either silica or alumina, or mixtures or compositions containing silica and alumina, or an aluminosilicate.

A process according to the present invention will remove oxides of nitrogen from a gas under either reducing or oxidising conditions. Under oxidising conditions, removal may occur either by decomposition or by selective reduction. Such a process represents a

-3-

considerable advance in the technology of purification of petrol and diesel exhaust gases and nitric acid tail gases.

According to a further feature of the invention, a process for the catalytic removal of oxides of nitrogen and the catalytic oxidation of carbon monoxide and hydrocarbons present in a gas comprises contacting the gas at elevated temperature with a catalyst comprising one or more metals of the platinum group supported on or associated with a refractory oxide, where "platinum group" and "refractory oxide" have meanings as defined above. In its most

10   important embodiment, the present invention provides a process for the catalytic reduction under oxidizing conditions for one or more oxides of nitrogen present in the exhaust from an internal combustion engine or from an industrial plant gas which comprises contacting the gas under oxidizing conditions at an elevated temperature with a metal catalyst comprising at least one metal selected from the group consisting of platinum, rhodium, and palladium metals supported on a particulate silica support, said particulate oxide support being itself deposited on a catalyst substrate.

20   Optionally, the catalyst may be associated with one or more other catalytic metals or metal oxides to assist in promoting the oxidation reaction.

Under certain circumstances, the catalytic decomposition of nitrogen oxides may lead to the formation of nitrous oxide. A further option, therefore, is that the catalyst be associated with one or more catalytic metals or oxides to promote the reduction or decomposition of nitrous oxide. We have found that oxides of one or more of lanthanum, cerium and titanium are particularly useful

for this purpose.

By "elevated temperature" we mean a temperature sufficient
for catalytic decomposition of a significant quantity of the oxide
of nitrogen etc. present or catalytic oxidation of a significant
quantity of the organic compound

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or carbon monoxide present to occur as a result of contact with a catalyst such as described above. In general, the elevated temperature would not exceed about 500-600°C. and, depending upon the exact nature of the catalyst, the optimum temperature could be in the region of 300-450°C.

The refractory oxide on which the catalytic metal or mixture of metals is deposited or with which it is associated, may be in the form of pellets, granules or powders but is preferably in the form of fine grains, the individual grains being typically slightly coarser than particles of powder.

10   An example of a suitable refractory oxide is Davison 70 (T.M.) silica.

The catalyst is optionally ultimately supported on a substrate known in the art. Examples of preferred substrates which may be used are porous refractory ceramic honeycombs or modules formed from corrugated metallic sheets rolled up to form a cellular structure. Other supports may be used, however, for example particulate solids such as granules, pellets, shapes and extrudates which can be constructed of ceramic or metallic refractory materials. Alternatively, the catalyst may be mixed with a catalytically inert refractory material, for example in the form of granules,

20   as an extender or diluent.

The ultimate supporting structure may have a first coating, layer or deposit of a refractory oxide

which may be the same as or different from the refractory oxide on which the catalytic metal is supported. This first refractory oxide is deposited on the ultimate support, preferably in the form of a film, and the film may have a thickness of 0.0004 to 0.001 inches.

Such oxides are calcined and preferably have a porous structure which has a relatively large internal pore volume and total surface area. Such oxides are referred to as "active", that is, catalytically active, refractory oxides.

Refractory oxides suitable for this purpose may be selected from the group consisting of silica, silumina, silica/alumina, titania, zirconia, magnesia, quartz and proprietary molecular sieve zeolites.

Catalysts for use in the process of the invention may be deposited directly on the support without the intervention of an intermediate refractory oxide layer. Such an arrangement includes a catalyst comprising a platinum group metal supported on or associated with, for example, silica and deposited on a ceramic or metallic ultimate support, so that, although no separate intermediate refractory oxide layer is included, the refractory oxide of the catalyst acts in lieu of such an intermediate layer.

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In addition to Davison 70 silica a range of colloidal suspensions sold under the trade mark SYTON by Monsanto may be used. For example, "Syton X30" which has a silica concentration of approximately 30%, has been used for applying silica to both ceramic and metallic monoliths prior to applying the precious metal.

The general procedure of preparation of such catalysts is to dip the monolith directly into the "Syton" solution, blow off the excess from the channels and surface of the monolith, dry and fire, and then to apply the precious metal by dipping into an aqueous solution of precious metal salt followed by drying and reducing in a stream of H_2/N_2. Metal supports (e.g. Fecralloy (T.M.) should be pre-oxidised by heating for 1 hour at $130^\circ C$. This has the effect of improving corrosion resistance to the gases with which the catalyst will come into contact and also improving the adhesion of the silica layer. Also, since metal supports, unlike ceramic supports, are not porous, two immersions in the silica sol, each followed by drying etc, are necessary to build up the desired coating of silica.

In detail, one method of applying a catalyst according to the invention on a ceramic support will now be described.

A ceramic honeycomb monolith (Corning M20 (T.M.)); 300 cells per square inch) made from cordierite and being in the shape of a cylinder 2 inches in diameter and 3 inches in length and therefore having a volume of 9.42 cu. ins. was immersed in 500 ml of Syton X30, the silica therein having a surface area in excess of 200 m2g-1, for 2 minutes. After withdrawal, the excess silica sol was first shaken off

- 7 -

and then blown off at an air pressure of 15 p.s.i. The weight of the monolith had increased from 92 to 108 g. The coated monolith was then dried at about $100^{\circ}C$ in a convection current of hot air flowing at > 300 ft.min.$^{-1}$ and was then roasted in a static kiln furnace at $500^{\circ}C$ for ½ hour. The resulting coated monolith weighed 97.2 g, hence the weight of silica was 5.2 g which represented a loading of 0.55 g.in^{-3}.

The film thickness represented by this loading falls within the range previously mentioned namely 0.0004 - 0.001 inch.

To deposit the precious metal on the silica, the following method was used:

The water absorption of the silica-coated monolith was measured and the amount of precious metal required to give a loading of 30 g.ft^{-3} of monolith was calculated. An aqueous solution of precious metal salt, for example, $RhCl_3.xH_2O$, at a concentration of 14 g.l^{-1} of Rh metal was made up and the silica-coated monolith immersed for 2 minutes in the solution, removed, allowed to drain and the excess salt solution blown off. The process was repeated, if and as necessary, until the predetermined weight, that is, of silica-coated monolith carrying the required quantity of solution corresponding to a metal loading of 30 g.ft^{-3}, was achieved. The process was completed by hot air drying and reduction in a tube furnace for one hour under an atmosphere of H_2/N_2 containing 5% H_2 at $450^{\circ}C$ (for rhodium) and $220^{\circ}C$ (for iridium).

Methods of deposition of oxide are described in

our British Patent Specification No. 1,390,182. Descriptions
of typical ceramic supports and useful metal supports which may
be used are given in British Patent Specification No. 882,484
(Corning) and in our published DOS No. 2,450,664.

The following descriptions, examples, tables and
figures are illustrative of the invention.

Preparation of the Catalysts

Catalysts comprising platinium, rhodium and iridium
supported on Davison 70 silica were prepared by impregnation of
the silica with a solution of the relevant chloride or acid
chloride of the required strength and volume. The impregnated
silica was then dried in vacuo (0.1 torr) at room temperature
and reduced in a stream of hydrogen at 350°C. (for platinum)
and 450°C. (for rhodium and iridium).

The following silica-supported catalyts were pre-
pared using the above method.

TABLE 1

Catalyst A	Rh/SiO$_2$	6.14×10^{-2}At%	(approx. 0.1 w/w%)
Catalyst B	Rh/SiO$_2$	6.14×10^{-3}At%	(approx. 0.1 w/w%)
Catalyst C	Pt/SiO$_2$	6.14×10^{-2}At%	(0.2 w/w%)
Catalyst D	Pt/SiO$_2$	6.14×10^{-3}At%	(0.02 w/w%)
Catalyst E	Ir/SiO$_2$	6.14×10^{-3}At%	(approx. 0.02 w/w%)

In the above table, atomic percentages are quoted as atoms of the metal calculated as a percentage of the number of moles of silica. In a similar way, weight percentages are expressed as weight of metal to weight of silica.

Experimental Test Rig

The experimental runs, results of which are given below, were carried out in a silica reactor comprising two concentric tubes mounted vertically. The outer tube had an o.d. of about 1¼" and the inner tube had an o.d. of about 3/8". The catalyst was carried on a bed of silica wool in the inner tube and the reaction gas stream was passed down the outer tube and up the inner. The gases were passed through a pre-heating zone upstream of the catalyst. Reactor gas inlet temperature was measured by means of a chrome-aluminel thermocouple located in a well below the catalyst. The reactor was surrounded by a heater equipped to give variable heating rates. The inlet and outlet concentration of gases was monitored using a BOC Luminox Analyser and Perkin-Elmer F17 gas chromatograph.

Experimental Results and Discussion

Two principal types of experiment were conducted on the catalysts. These were:

(a) a profile of activity in removal of oxides of nitrogen versus inlet temperature at a fixed ratio of oxidising to reducing species in the inlet gas stream; and

(b) an isothermal profile of activity against ratio at a temperature chosen from the result of experiment type (i).

The ratio (R) of oxidising to reducing species in the inlet gas stream is calculated according to the equation

- 10 -

$$R = \frac{2 \cdot x \; \%O_2 + \% NOx}{\% CO}$$

Generally, the particular oxide of nitrogen (NOx) in the equation is nitric oxide, NO.

In the experiments described below, the weight of catalyst tested was generally 1 g. In some experiments, smaller weights were tested, typically 0.005 g., but in all experiments using less than 1 g. of catalyst, pure silica was added as an extender to the catalyst to give a total weight of 1 g. in order to prevent bed fluidisation.

Space velocity was calculated on the basis of catalyst weight exclusive of the weight of added pure silica, if present, and is quoted in units of hr^{-1}.

Experimental runs were conducted as in the following table (Table 2) in which the "Catalyst" designation refers to Table 1, the "Experimental type" refers either to (a) or (b) as above, and the "R or temperature" refers to the fixed ratio R (for experimental type (a)) or to the isothermal temperature (for experimental type (b)).

- 11 -

TABLE 2

Run No. (also Fig.No.)	Catalyst	Wt. of Catalyst	Wt. of added SiO_2	Space velocity	Experimental Type	R or Temp.
1	A	1g	-	2,200	a	1.9
2	A	0.005g	0.995g	440,000	a	1.9
3	A	0.005g	0.995g	440,000	b	395°C
4	B	1g	-	2,200	a	1.9
5	B	1g	-	2,200	b	325°C
6	C	1g	-	2,200	a	1.9
7	C	0.005g	0.995g	440,000	a	1.9
8	C	0.005g	0.995g	440,000	b	400°C
9	D	1g	-	2,200	a	1.9
10	D	1g	-	2,200	b	360°C
11	E	1g	-	2,200	a	1.9
12	E	1g	-	2,200	a	1.9
13	E	1g	-	2,200	B	329°C

* Run 12 was repeat of Run 11 using the identical catalyst.

Run 1 shows the activity of a Rh/SiO_2 catalyst at an R value of 1.9 (i.e. oxidising conditions). NOx decomposition showed a maximum of 95% at about 230°C. and the "half peak activity range" (that is, the active temperature range at half the maximum activity) was 220°C. Nitrous oxide formation (as a percentage of the total NOx input) reaches a maximum just above the NOx decomposition threshold temperature and decreases steadily to zero at about 450°C.

Run 2 was carried out under similar conditions to Run 1 using the same catalyst, except that the actual catalyst weight was 0.005g. instead of 1g. The effect of this was to raise the temperature of maximum activity to 400°C. At this temperature, decomposition of NOx is still 75% despite the small amount of catalyst and the correspondingly high space velocity compared with Run 1. Formation of N_2O did not rise above 18% and, at the temperature of maximum decomposition of NOx, was already dropping rapidly.

Run 3 was carried out using the same catalyst as Run 2 but under isothermal conditions, a temperature near the maximum activity of NOx decomposition from Run 2 being selected (395°C.). Maximum NOx decomposition (and minimum N_2O formation) occurred at about the stoichiometric point (R=1) and the value of R at 50% of the maximum NOx decomposition was 2.8.

Run 4 used 1g. of a Rh/SiO_2 catalyst of lower metal loading compared to Runs 1, 2 and 3. Diluting the metal loading results in a lower maximum of NOx decomposition at a higher temperature, and also a lower half-peak activity of 160°C.

Run 5 - the isothermal plot using the catalyst of Run 4 - showed that the catalyst was less resistant to oxygen poisoning between R values of about 1 and 5 and that production of N_2O was higher than with the

- 13 -

similar catalyst of higher metal loading. The value of R at 50% of maximum NOx decomposition was 2.5.

Run 6 used 1g. of a Pt/SiO_2 catalyst and is comparable to Run 1 using a similarly loaded Rh/SiO_2 catalyst. The results of Run 6 indicated that the maximum activity in NOx decomposition for Pt/SiO_2 was only 50% compared with 95% for Rh/SiO_2. However, this poor result does not necessarily reflect accurately the true activity of this catalyst since little is known as yet about the relative dispersions of the metals on silica. The half-peak activity for Pt/SiO_2 was $200^\circ C$. compared to $220^\circ C$. for Rh/SiO_2.

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Run 7 used 0.005g. of the same catalyst and is therefore comparable to Run 2. As in Run 2, lowering the quantity of catalyst increased the temperature of maximum activity in NOx decomposition but the maximum decomposition was only 17%.

Run 8 was carried out under isothermal conditions at a temperature of $400^\circ C$. Compared to Run 3 (using Rh/SiO_2 catalyst) the resistance to oxygen poisoning was poor. The value of R at 50% of maximum NOx decomposition was 1.25.

Run 9 was carried out using 1g. of a Pt/SiO_2 catalyst having a lower metal loading than that used in Runs 7 and 8. Run 9 therefore compares

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with Run 4 for Rh/SiO_2 and the results show that Pt/SiO_2 is inferior to Rh/SiO_2 in respect of NOx decomposition and about the same for half peak activity.

Run 10 was carried out under isothermal conditions at a temperature of $360^\circ C$. Again, comparing the results with Run 5, Pt/SiO_2 shows less resistance to oxygen poisoning than does Rh/SiO_2. The value of R at 50% of maximum NOx decomposition was 1.7.

Run 11 used an Ir/SiO_2 catalyst and compares with Run 4 (Rh/SiO_2)

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- 14 -

and Run 9 (Pt/SiO$_2$). Maximum Nox decomposition was 65% at 345°C. and at this temperature production of N$_2$O was virtually zero. Half peak activity was 190°C.

Run 12 was a re-run of Run 11, using the identical catalyst, and shows the remarkable effect of heating to 600°C. in Run 11. Maximum Nox decomposition was 90% at a temperature of 350°C. and production of N$_2$O was still extremely low, peaking at 2%. The half peak range was comparatively sharp at 100°C.

Run 13, the isothermal experiment on Ir/SiO$_2$ at 329°C., shows
10   that this catalyst is considerably more resistant to oxygen poisoning than either Rh/SiO$_2$ (Run 5) or Pt/SiO$_2$ (Run 10). The value of R at 50% of maximum NOx decomposition was 5. N$_2$O production is consistently either very low or zero throughout the entire range of R.

In conclusion, it may readily be seen that these catalysts show remarkable results for the decomposition of NOx under oxidising conditions. Furthermore, all of them showed high efficiency in the oxidation of carbon monoxide and it is anticipated that these catalyst, either alone or in association with known oxidation catalyst, for example alloys of the precious metals such as Pt/Rh, will successfully oxidise the lower hydrocarbons typically
20   present in the exhaust gas stream from an internal combustion engine.

Rh/SiO$_2$ and Pt/SiO$_2$ tended under certain conditions to cause the formation of nitrous oxide. We have found that certain additives may be incorporated or admixed with the catalysts to catalyse the reduction or decomposition of nitrous oxide. Examples of such additives are oxides of lanthanum, cerium and titanium.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the catalytic reduction under oxidizing conditions of one or more oxides of nitrogen present in the exhaust from an internal combustion engine or from an industrial plant gas which comprises contacting the gas under oxidizing conditions at an elevated temperature with a metal catalyst comprising at least one metal selected from the group consisting of platinum, rhodium, and palladium metals supported on a particulate silica support, said particulate oxide support being itself deposited on a catalyst substrate.

2. A process according to claim 1 wherein the metals are present in the form of an alloy or as a mixture.

3. A process according to claim 1 or claim 2 wherein the catalyst includes one or more base metals or one or more precious metals not specified in claim 1.

4. A process according to claim 1 wherein the catalyst includes at least one additional metal or oxide for promoting the reduction of nitrogen oxide.

5. A process according to claim 4 wherein the oxide is an oxide of at least one of lanthanum, cerium and titanium.

6. A process according to claim 1 wherein the gas is automobile exhaust gas.

7. A process according to claim 1 wherein the substrate is made from a refractory oxide in the form of a honeycomb.

8. A process according to claim 1 wherein the substrate is made from a metallic sheet material in the form of a cellular structure.

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9.   A process according to claim 1 wherein the elevated temperature is within the range 500-600°C.

10.   A process according to claim 9 wherein the elevated temperature is within the range 300-450°C.

17